Patent Claims

1. Process for producing defined layers or layer systems of polymers or oligomers with controlled structure on arbitrary solid surfaces, wherein the layers are chemically applied to the solid surface by means of "living"/controlled free radical polymerisation by the following steps:

a) binding the initiators of the general Formula 1 to the solid surface by means of a primary valency bond via the anchor group A, the solid used already having chemical properties on its surface or it being possible to generate chemical properties thereon,

A-L-I

1

where A is an anchor group, I is the group acting as initiator for the ATRP polymerisation and L is the connecting link between A and I, I is the structural element C-Z' and Z' is selected from the group comprising Cl, Br, I, OR^{10}, SR^{14}, SeR^{14}, -SCN, $OC(=O)R^{14}$, $OP(=O)R^{14}$, $OP(=O)(OR^{14})_2$, $OP(=O)OR^{14}$, $O\text{-}N(R^{14})_2$ and $S\text{-}C(=S)N(R^{14})_2$; where R^{14} is aryl, linear or branched C_1 to C_{20} alkyl, preferably C_1 to C_{10} alkyl, or if an $N(R^{14})_2$ group is present, the two R^{14} groups together can form a five-, six-, or seven-membered heterocyclic ring; and where R^{10} is C_1 to C_{20} alkyl, where each H atom independently of one another can be replaced by halogen, preferably fluoride (sic) or chloride (sic), C_2 to C_{20} alkenyl, preferably vinyl, C_2 to C_{10} alkynyl, preferably acetylinyl, phenyl, which is [lacuna] by 1 to 5 halogen atoms, by C_1 to C_4 alkyl or by an aralkyl group, where the aryl group is preferably phenyl or substituted phenyl and the alkyl group is a C_1 to C_6 alkyl group;

"aryl" is phenyl, naphthyl, phenanthryl, phenalenyl, anthracenyl, triphenylenyl, fluorenyl, fluoranthenyl, pyrenyl, pentacenyl, chrysenyl, naphthacenyl, hexaphenyl, picenyl and perylenyl (preferably phenyl and naphthyl), where each hydrogen atom can be replaced by C_1 to C_{20} alkyl (preferably C_1 to C_6 and particularly preferentially methyl), C_1 to C_{20} alkyl (preferably C_1 to C_6 and particularly preferentially methyl), where each of the hydrogen atoms is

independently replaced by halogen (preferably fluorine or chlorine), C_2 to C_{20} alkenyl, C_1 to C_{20} alkynyl, C_1 to C_6 alkoxy, C_1 to C_6 alkylthio, C_3 to C_8 cycloalkyl, phenyl, halogen, NH_2, C_1 to C_6 alkylamino, C_1 to C_6 dialkylamino and phenyl, which can be substituted by from 1 to 5 halogen atoms and/ or C_1 to C_4 alkyl groups;

this definition of "aryl" is also to be applied to the aryl groups in "aryloxy" and "aralkyl". (sic) Accordingly, phenyl can be mono- to penta-substituted and naphthyl can be mono- to hepta-substituted by an above substituent (if one of the aryl groups is substituted, it is preferably mono- to tri-substituted). (sic) Particularly preferentially "aryl" relates to phenyl, naphthyl, phenyl which is mono- to penta-substituted by fluorine or chlorine and phenyl which is mono- to tri-substituted by substituents selected from the group comprising C_1 to C_6 alkyl, C_1 to C_4 alkoxy and phenyl.(sic) Particularly preferentially "aryl" relates to phenyl and tolyl;

the binding to the solid surface via a primary valency bond of **1** via the anchor group A is to be so chosen that it is stable under the selected ATRP-conditions. (sic) The group I is to be so chosen that ATRP can be carried out below 120 °C;

the only prerequisite as far as the solid to be used is concerned is that it already exhibits chemical properties on its surface or that chemical properties which allow the binding of chemical compounds via primary valency bonds can be produced thereon; here the term "primary valency bond" is to be understood as the entire spectrum of chemical bonds covered by the three limiting cases of covalent, ionic and metallic bond as well as the transitions between the three limiting cases,

b) carrying out a "live"/controlled free radical polymerisation in accordance with the ATRP (Atom Transfer Radical Polymerisation) mechanism at temperatures of below 120 °C, by reaction of the initiator group I with monomers or macromonomers capable of free radical polymerisation or with mixtures thereof, by which means the polymer layer is produced on the solid surface.

2. Process according to Claim 1, characterised in that subsequent to step a) the step b) is carried out several times in order to produce a second or further polymer layers on the first polymer layer.

3. Process according to Claim 1 or 2, characterised in that the polymer layers are modified by chemical conversion, by means of suitable reactants, of functional groups of the oligomer or polymer chains bonded to the solid, while maintaining the degree of polymerisation.

4. Process according to Claims 1 to 3, characterised in that the solid-polymer layer systems produced can be chemically bound in a three-dimensional polymer matrix by crosslinking reactions.

5. Process according to Claims 1 to 4, characterised in that the solid is of natural or synthetic origin.

6. Process according to Claims 1 to 5, characterised in that the solid surface can consist of any desired material.

7. Process according to Claims 1 to 6, characterised in that the solid can be in solid, porous or finely divided form.

8. Process according to Claims 1 to 7, characterised in that the surface structure of the solid can be heterogeneous.

9. Process according to Claims 1 to 8, characterised in that the surface composition of the solid can be heterogeneous.

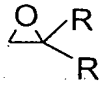
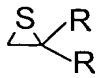
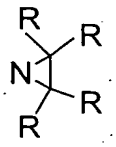
10. Process still (sic) Claims 1 to 9, characterised in that the initiators used are those of the following formula 1

A-L-I

1

where A is an anchor group which permits the binding to a solid surface via a primary valency bond. (sic) As defined in Claim 1, the term primary valency bond is to be understood to mean the entire spectrum of chemical bonds. (sic) The linkages between anchor group and solid surface can be established by condensation, substitution or addition reactions, or by the interaction between counterions. (sic)

A can, for example, be one of the following functional groups:

OH	$CO\text{-}CH=CR_2$	NR-OH	PO_3^-	SO_2Cl
Halogen	$CO\text{-}NR_2$	$NH\text{-}C(NR)\text{-}NH_2$	$O\text{-}PO_2Cl$	SOCl
$SiR^3_yR^4_zX_{3-(y+z)}$*)	C≡N	$CO\text{-}NR\text{-}NR_2$	PO_2Cl	
CR=CR **)	NH-C≡N	$CH=CR\text{-}NR_2$	COSR	
$CR=CR_2$	NH_2	CO-N=C=S	CSOR	
C≡CR	NHR	N=C=O	$CS\text{-}NR_2$	
CRO	NR_2	N=C=S	CSSR	
COOR	NH_3^+	O-C≡N	SH	
COO^-	NH_2R^+	S-C≡N	SO_3R	
COCl (Br)	NHR_2^+	NO_3^-	SO_2R	
CO-O-CO-R	NH-COOR	$N^+≡N$	SOR	
CH(OH)(OR)	$C(NR)\text{-}CH=CR_2$	$N=P(phenyl)_3$	SO_3Cl	
$C(OR)_3$	$NR\text{-}NR_2$	$CH=P(phenyl)_3$	SO_3^-	

*) X = halogen, OR^6, NH_2, with R^6 as well as R^3 and R^4 = alkyl, including branched, preferably methyl, ethyl, including unsaturated, also cycloalkyl, preferably cyclohexyl, including substituted, aryl, preferably phenyl, including substituted, $(y+z)\leq 2$

**) R = a substituent, in each case independently selected from the group comprising: H, alkyl, preferably methyl to propyl, aryl, including substituted,

preferably phenyl, also mixed alkyl and aryl; applies in respect of all R in this table that have no labels.

or

the anchor group A can be a metal radical M, with which A-L becomes a group in the sense of an organometallic reagent M-L. (sic) In a chemically meaningful manner, matched to L and also matched to the type of the functional groups on the solid surface, via which the reaction with the anchor group A = M is to be carried out, M is so chosen that crosslinking reactions can be carried out with the reactants M-L and functional groups on the solid surface. (sic) M-L can thus be organometallic groups containing lithium (Murahashi), sodium, magnesium (Grignard, Kumada-Tameo, Corriu), boron (Suzuki-Miyaura), aluminium (Nozaki-Oshima, Negishi), zirconium (Negishi), zinc (Negishi, Normant) copper or copper-lithium or copper-zinc (Normant, Sonogashira), tin (Migita-Kosugi, Stille), silicon (also variants of Hiyama), mercury, cadmium and silver;

and where L is selected from the following group containing (sic)

1. L is a structural element which according to formula $R^{11}R^{12}R^{13}C$-Z' possesses the groups R^{11}, R^{12}, R^{13}, which are defined further below and in each case are selected independently of one another, where at least one H or halogen in all three, preferably in two, but particularly preferentially in one of the groups R^{11}, R^{12}, R^{13} is A and the groups R^{11}, R^{12}, R^{13} are to be selected accordingly. (sic) Furthermore, at least one (optionally present) H or halogen in all three, only in two or also only in one of the groups R^{11}, R^{12}, R^{13} can also be I. (sic) Here functional groups, which are encompassed by the variability of R^{11}, R^{12}, R^{13}, can already perform the function of anchor groups A or they can serve for the introduction of A;
R^{11}, R^{12} and R^{13} are in each case independently selected from the group comprising H (no more than two of R^{11}, R^{12} and R^{13} are H, preferably no more

than one of R^{11}, R^{12} and R^{13} is H), halogen, C_1 to C_{20} alkyl (preferably C_1 to C_{10} alkyl and particularly preferentially C_1 to C_6 alkyl), C_3 to C_9 cylcoalkyl, $C(=Y')R^5$, $C(=Y')NR^{6'}R^{7'}$ (where Y', R^5, $R^{6'}$ and $R^{7'}$ are as defined further below), COCl, OH (preferably only one of R^{11}, R^{12} and R^{13} is OH), CN, C_2 to C_{20} alkenyl or alkynyl (preferably C_2 to C_6 alkenyl or alkynyl and particularly preferentially vinyl), oxiranyl, glycidyl, aryl, heterocyclyl (where "aryl" is as defined in Claim 1 and "heterocyclyl" is defined further below), aralkyl, aralkenyl (aryl-substituted alkenyl, where alkenyl is vinyl, which can be substituted by one or two C_1 to C_6 alkyl groups and/or halogen atoms, preferably chlorine), C_1 to C_6 alkyl where from 1 to all hydrogen atoms (preferably 1) have been replaced by halogen (preferably fluorine or chlorine if 1 or more hydrogen atoms have been replaced and preferably fluorine, chlorine or bromine if 1 hydrogen has been replaced) and C_1 to C_6 alkyl, which is substituted by from 1 to 3 substituents (preferably 1), which have been selected from the group consisting of C_1 to C_4 alkoxy, aryl, heterocyclyl, $C(=Y')R^5$, $C(=Y')NR^{6'}R^{7'}$ (where Y', R^5, $R^{6'}$ and $R^{7'}$ are as defined below), oxiranyl and glycidyl;

in the above group definitions Y' = $NR^{8'}$ or O; R^5 = C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, aryloxy or heterocyclyloxy; $R^{6'}$ and $R^{7'}$ are in each case independently H or C_1 to C_{20} alkyl or $R^{6'}$ and $R^{7'}$ can be joined to give a C_2 to C_5 alkylene group and thus form a three- to five-membered ring; $R^{8'}$ = H, linear or branched C_1 to C_{20} alkyl or aryl;

"heterocyclyl" relates to pyridyl, furyl, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl, indoyl, isoindoyl, indazoyl, benzofuryl, isobenzofuryl, benzothienyl, isobenzothienyl, chromanyl, xanthenyl, purinyl, pteridinyl, quinolyl, isoquinolyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, phenoxathiinyl, carbazolyl, cinnolinyl, phenathridinyl, acryidinyl, 1,10-phenathrolinyl, phenazinyl, phenoxazinyl, phenothiazinyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, as well as the hydrated forms thereof, which are known to those skilled in the art; preferred heterocyclyl groups encompass, pyridyl, furyl, pyrrolyl, thienyl imidazolyl,

pyrazolyl, pyrazinyl, primidinyl, pyridazinyl, pyranyl and indolyl, pyridyl being the particularly preferred heterocyclyl group. (sic)

2. L is a structural element, in which all groups R^{11}, R^{12}, R^{13} in formula $R^{11}R^{12}R^{13}C\text{-}Z'$, or two of these groups or even only one group, have been replaced by

a) oligo(oxyalkylene) with C_1 to C_{20}, also alternating C_1 and C_2 groups,

b) oligo(ethyleneimine),

c) oligosiloxanyl with Si_1 to Si_{20}, SiR^1R^2 with R^1 and R^2 being alkyl, preferably methyl, also aryl, preferably phenyl, also mixed alkyl and aryl,

where in a) to c) at least one H, in c) at least one H or also at least one aryl is A in all three, preferably in two, but particularly preferentially in one of the groups R^{11}, R^{12}, R^{13}. (sic) Moreover, in a) to c) at least one H or in c) at least one H or one aryl can also be I in all three, only in two or also only in one of the groups R^{11}, R^{12}, R^{13}. (sic)

3. L is a structural element, in which a group R^5 optionally contained in the groups R^{11}, R^{12}, R^{13} is, going beyond the above specification, one of the following groups:

a) oligo(oxyalkylene) with C_1 to C_{20}, also alternating C_1 and C_2 groups,

b) oligo(ethyleneimine),

c) oligosiloxanyl with Si_1 to Si_{20}, SiR^1R^2 with R^1 and R^2 being alkyl, preferably methyl, also aryl, preferably phenyl, also mixed alkyl and aryl,

where in a) to c) at least one H, in c) at least H or also at least one aryl is A in all three, preferably in two, but particularly preferentially in one of the groups R^{11}, R^{12}, R^{13}. (sic) Moreover, in a) to c) at least one H or in c) at least one H or one aryl can also be I in all three, only in two or also only in one of the groups R^{11}, R^{12}, R^{13};

The (sic) appropriate choice of L offers, via functional groups contained therein, the possibility of the splitting off the polymer layer from the solid surface. (sic)

and where I is selected from the group

C-Z' according to formula $R^{11}R^{12}R^{13}$ C-Z', where Z' has been selected from the group (sic) defined in Claim 1. (sic)

and where A, L, and I can each independently be freely chosen from the specifications given above for A, L, and I.

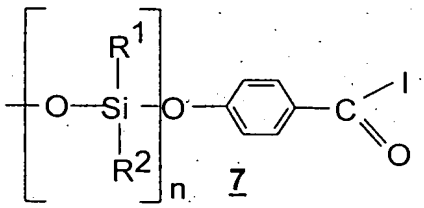
11. Process according to Claim 10, characterised in that the initiators used are those of the formulae **2** - **6**

$X_{3-(y+z)}R^3_yR^4_zSi–L–I$ (**2**) $Y–CO–L–I$ (**3**) $HS–L–I$ (**4**) $I–L–S–S–L–I$ (**5**) $=–L–I$ (**6**)

where I is specified in Claim 1 and L in Claim 10
and X is selected from the group comprising halogen, OR^6, NH_2
and R^6, R^3, R^4 are selected from the group comprising alkyl, including branched, preferably methyl, ethyl, including unsaturated, also cycloalkyl, preferably cyclohexyl, including substituted, aryl, preferably phenyl, including substituted;
and Y is selected from the group comprising halogen, preferably chlorine or bromine, OH, OR^7, where R^7 = alkyl, preferably methyl or ethyl, aryl, preferably phenyl, including substituted, aralkyl, preferably benzyl, acyl, aliphatic or aromatic, trialkylsilyl, preferably trimethylsilyl;
and y = 0, 1, 2 and z = 0, 1, 2 and $(y+z) \leq 2$.

12. Process according to Claim 10 or 11, characterised in that in the case of advantageous selection of L the initiators used are those in which L has been chosen as a chemical bond, alkyl with C_1 to C_{20}, preferably C_1 to C_8; aryl, preferably phenyl, including substituted; aralkyl with the aryl component preferably phenyl and with the alkyl component C_1 to C_{20};

or as a structural element, with which compounds of the formulae **7** to **11** result as initiators:



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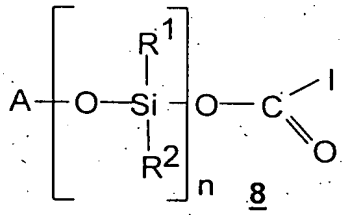

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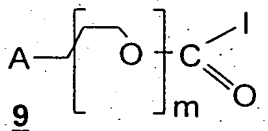

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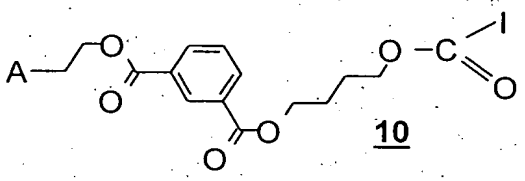

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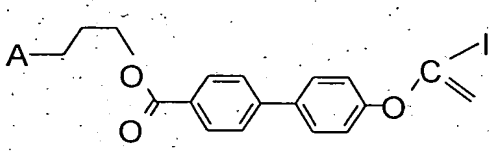

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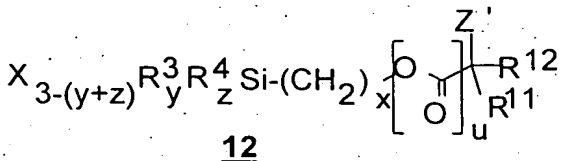
where I is specified in Claim 1 and A in Claim 10
and R^1, R^2 are selected from the group comprising alkyl, preferably methyl, also aryl, preferably phenyl, including substituted, also mixed alkyl and aryl; and n = 1 - 20 and m = 1 - 20.

13. Process according to Claims 10 to 12, characterised in that the initiators used are those of the formulae **12** - **28**



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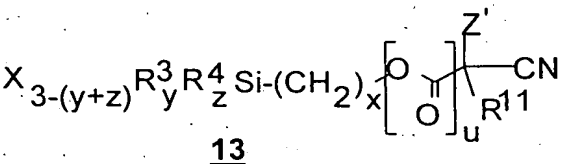

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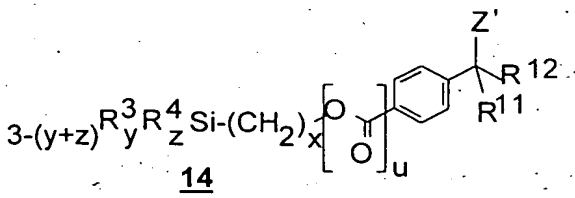

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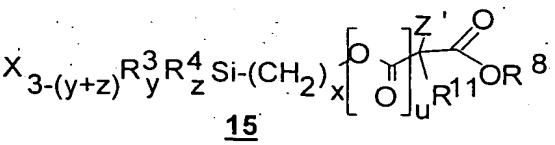

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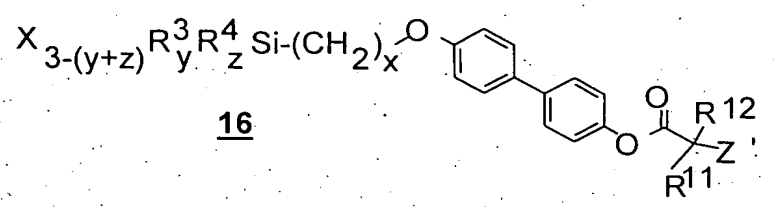

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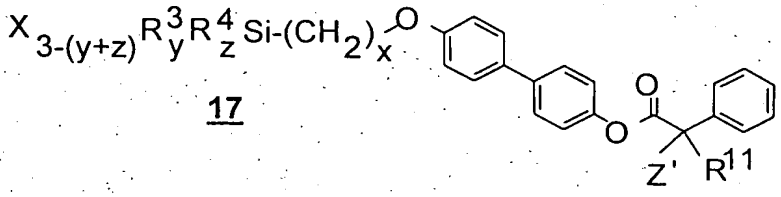

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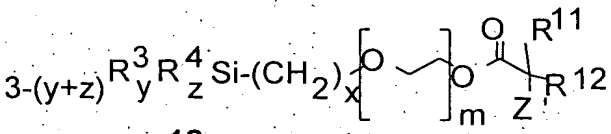

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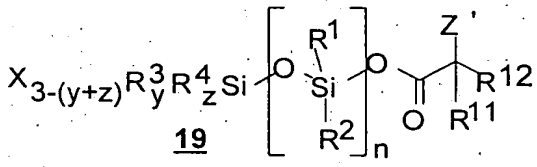

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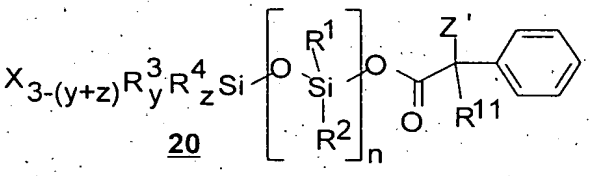

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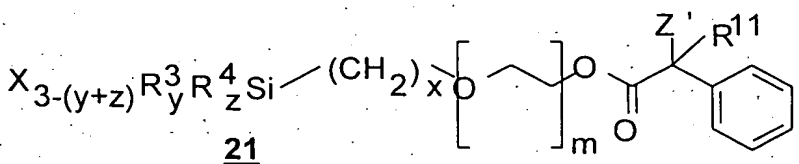

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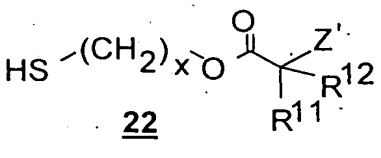

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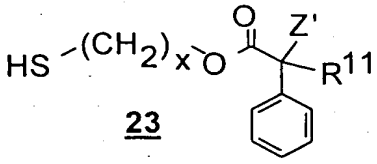

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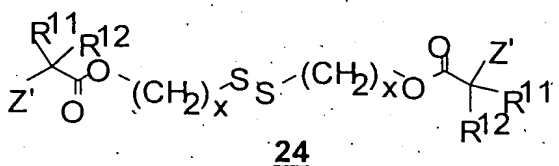

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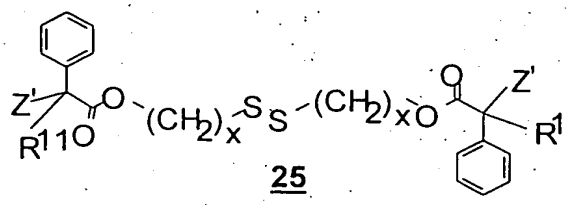

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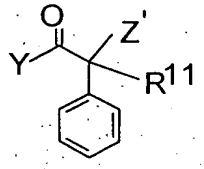

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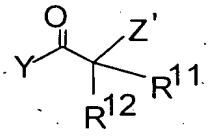

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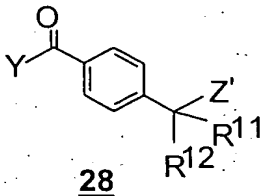

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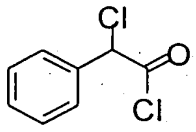
where Z' is specified in Claim 1, y, z, X, R^1, R^2, R^3, R^4, R^{11}, R^{12} are specified in Claim 10, Y is specified in Claim 11 and n, m are specified in Claim 12

and x = 1 - 20

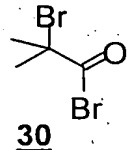
and u = 0, 1

and R^8 is selected from the group comprising H, alkyl, preferably methyl, ethyl.

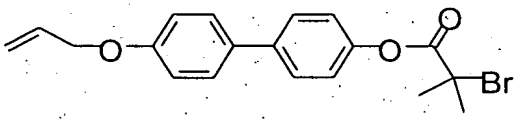
14. Process according to Claims 10 to 13, characterised in that the initiators used are those of the formulae **29** - **39**



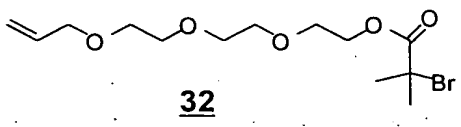
29



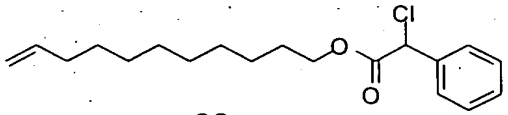
30



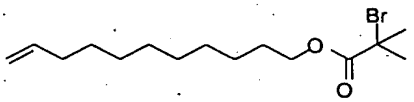
31



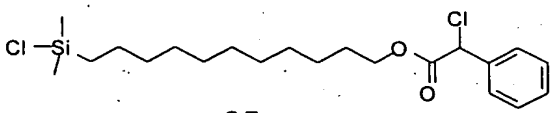
32



33



34



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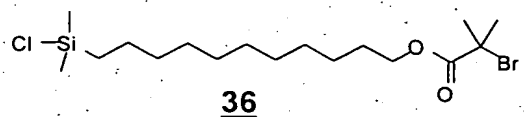

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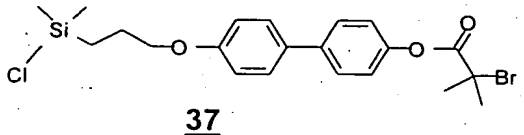

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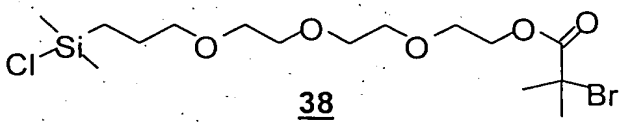

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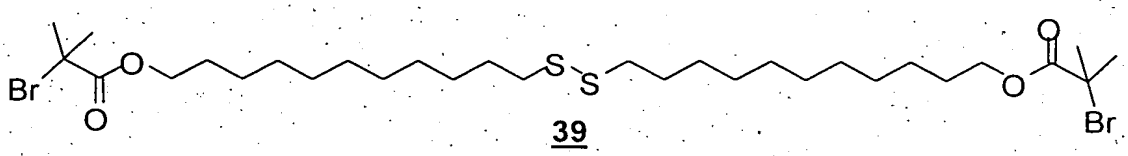

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15. Solid surface with oligomer or polymer layers, produced in accordance with the process according to Claims 1 to 10.